Refining and Use of Byproducts from Various Fats and Oils

The following was written by Imre L. Balazs, Central Soya Co. Inc., Research and Engineering Center, based on his presentation at the 36th Oilseed Processing Clinic held in March in New Orleans, Louisiana.

There are several factors that affect finished products as well as refinery byproducts from various fats and oils. These include (a) the quality of the fat- or oil-bearing materials, (b) their storage conditions and (c) processing methods to recover and refine the triglycerides.

The quantity and quality of byproducts can vary over a very wide range. To minimize the yield and to influence the quality of byproducts, fats and oils must be protected from oxidation and from conditions that promote decomposition of triglycerides and phosphatides during storage and handling.

REFINING METHODS

Refining methods commonly used today are caustic and physical refining. Caustic refining is a process that can be adjusted to almost every oil and fat quality the processor must refine. Caustic refining removes gums more completely than does degumming and at the same time neutralizes the free fatty acids and reduces the level of trace metals, color bodies and some oxidation products present in the crude oil.

The challenge for the refinery operator is to obtain the desired refined oil quality at a minimum loss of neutral oil into the soapstock. To accomplish this, a properly designed plant is needed that suits the characteristics of the crude oil or fat. There are several methods of refining: long-mix, multi-mix, miscella refining and cold refining-dewaxing. Selecting the proper equipment and applying optimum treatment level and chemical strength are all important. Reaction time and centrifugation temperatures must be properly set and the backpressure adjusted to optimize the separation efficiency of the primary centrifuge. After the soapstock is separated from the oil, the oil usually is washed with water.

Physical or steam refining is a process that can remove volatile compounds from fats and oils through high temperatures and high vacuum conditions while live steam is injected into the oil. Of course, nonvolatile impurities that negatively affect finished product quality must be removed from the fat or oil prior to steam refining.

A number of process steps normally are needed in both refining methods to assure good quality finished products and byproducts. Caustic refining includes five process steps, one of them optional: degumming (optional), neutralization, water washing, bleaching and deodorization. Byproducts produced are lecithin sludge, soapstock, wash water, oil in spent clay and distillate. Process steps in physical refining are degumming, bleaching and steam refining. Byproducts are lecithin sludge, oil in spent clay and distillate. Degumming, or rather desludging, of certain fats will not result in a regular lecithin gum, as is the case with many soft oils.

Degumming is one process step that has undergone a number of modifications to achieve better lecithin removal from the oil. Traditional water degumming is used to recover lecithin gums for manufacturing lecithin products or to remove gums that would interfere with subsequent operations, such as storage or acidulation of the soapstock when nondegummed oil is being refined.

Conditioning soybean flakes prior to extraction with live steam produces crude oil that can be degummed with water using two centrifuges in a series to obtain degummed oil that can be physically refined after bleaching. This process yields an increased amount of lecithin with somewhat higher phosphatidylcholine content than is found in conventional lecithins. Pretreatment of soybean oil with acetic acid anhydride prior to degumming is another method yielding oil containing low levels of residual phosphatides compared to water-degummed oils.

The lecithin gums recovered by these methods can be used for making finished lecithin products. The following degumming methods yield gums that may not be utilized for manufacturing lecithin products:

- Cold degumming process—removes most of the waxes along with the lecithin but at the expense of higher oil loss.
- Superdegumming method—used when preparing seed oils for either physical or low-loss caustic refining. Since the oil is treated with citric acid, the recovered gums might not be suitable for manufacturing certain lecithin products.

For palm and lauric acid-type oils and animal fats, acid and dry degumming were developed mainly for reducing trace metals and proteinaceous material contents prior to bleaching and steam refining.

For edible and certain industrial applications of lecithin products, the oil prior to water degumming must be freed of all insoluble impurities. Natural lecithins, as well as chemically modified, fractionated and blended products, have an almost endless list of applications. About 100 different lecithin products are manufactured worldwide. The total volume of the lecithin or lecithin-based products is estimated at 250 million pounds per year.

The gums not wanted or unsuitable for making edible or industrial lecithin products can be added back to the meal or used as feed ingredients in conjunction with feed fats. Feeding studies indicate that lecithin compounds, in addition to giving nutritive value, improve the utilization of feed fats added as an energy source for the animals.

Caustic refining generates two side streams: soapstock and wash water. In miscella refining, washing is normally not necessary. The quantity and composition of the soapstock depend upon the quality and type of feedstock. The value of the soapstock is determined by its total fatty acid content. It is very important to the refiner to use the soapstock in the most cost-effective manner. The traditional fatty acid recovery process—acidulation—yields acid water for disposal.

The location of many refineries has caused environmental problems in disposing of the wash water. This problem is greatly amplified if strict regulations limit the phosphorus content of the effluent.

Under certain circumstances, acidulation of the soapstock is not economically justifiable. If that is the case, other uses must be found. Some methods not requiring acidulation are:

- Adding the soapstock back to the meal ahead of the meal drying unit. Even distribution of the soapstock is important to avoid high sodium concentrations.
- Selling the soapstock to soap manufacturers or to other customers. Formaldehyde may be added to prevent fermentation or molding during shipment.
- Adjusting the pH of the soapstock with mineral acid to 5 to 6, draining the settled water and selling it as neutralized wet soapstock. Rendering plants can use this material in their animal/vegetable feed fat product.
- Neutralizing the soapstock to about a pH of 6.5 with mineral acid, then evaporating the water under vacuum. The neutralized, wetted soapstock can be used as feed fat, especially in poultry feed because it contains pigments. Its level of use, however, is limited due to a high sodium content. This material is difficult to handle at the feed mill.
- Completing the saponification of neutral oil present in the soapstock. Water-insoluble metallic soaps are precipitated by adding water-soluble salt of the selected metal. Metallic salts of fatty acids are incorporated as ingredients in many products, including lubricants, cosmetics and certain animal feeds. Evaporative crystallization or concentration of the salts present in the water phase may be done if economically justifiable. This is similar to the neutralized dried soapstock process, only nonpolluting water vapors are generated.

These disposal methods should be used for soapstocks with high solid content; the only exception is the last process mentioned.

The wash water on hand can be acidulated, and disposal problems can be minimized. Waste oils from other sources can be added to the wash water and purified in the acidulation process.

SOAPSTOCK ACIDULATION

The basic acidulation process consists of three steps. The first is to react the soap-wash water mixture with excess acid to assure that the reaction is complete. The second is to separate the acid oil from the acidic water. The third is the neutralization of the acid water. However, if the soapstock contains a large percentage of phosphatides (as is the case for refining nondegumming soybean oil), the basic acidulation process must be modified to include a saponification step, and the reaction between the acid and soapstock should be completed in an agitated pressure vessel at elevated temperatures.

In addition to the traditional batch process, several continuous processes have been developed. Some of these methods use centrifuge to cause oil/water separation. Others use settling basins or tanks. Centrifuge use has not been widely accepted in the U.S.

Organic matter left in the water is readily biodegradable, but the treatment facilities are expensive to construct and operate. Where lime treatment and other precipitating agents must be used to reduce phosphorus, the cost of wastewater treatment sharply increases; also, the sludge presents a disposal problem.

ACID OIL USE

Since about 1950, the animal feed industry has used vegetable fats in its products directly or blended with animal fats. Acid oil is one of the main raw materials. The quantities and types of acid oils available for feed use are directly related to the usage of refined vegetable oils. Acid oil recovered from soybean soapstock is by far the largest type available. Individual feed manufacturers purchase refinery byproducts such as acid oil according to their own quality specifications to meet specific needs. For example, minimum and maximum iodine values may be established. Otherwise, the accepted quality specifications for feed grade vegetable fat are 90% minimum total fatty acids, 50% maximum free fatty acids, 1.5% maximum moisture, 1% maximum impurities, 4% maximum unsaponifiables and 6% maximum total MIU (moisture, impurities and unsaponifiables).

If the feed fat is to be used in layer, breeder or broiler rations, no cottonseed oil byproduct should be included. Fats also must be certified that any polychlorinated biphenyl (PCB) and pesticide residues are within allowable limits, and poultry feed fats should be certified as negative for chick edema factor.

The energy cost relationship between feed fats and corn could have an effect on fat levels in feeds. Fats added to carriers, the so-called dry fats, are expected to help the increased use of fats in feeds by providing easy handling, especially when complete feeds are blended on the farm.

Fatty acids from both animal and vegetable origins have many valuable and diverse end uses. Byproducts from refining edible fats and oils could be used as starting material for fatty acid production. The free fatty acid content determines if the acid oil can go directly to the distillation process or if its triglyceride content first should be hydrolyzed in a fat splitting process. The recovered sweet water containing some glycerol goes to the glycerol recovery system, and the crude fatty acids might be used in low-cost oleochemical soaps, industrial cleaners and cutting oils. If color, odor and certain impurities would interfere with the intended application, the mixed fatty acids can be purified in a straight distillation process. To separate fatty acids by their unsaturation or melting point, several fractionation methods have been developed. These methods involve crystallization and separation of solids from the liquid phase with or without using solvents or aqueous solutions. Fractional distillation is a separation method in which fatty acids can be separated by their boiling point.

The fatty acid composition of acid oils might be altered by hydrogenation. Distilled unsaturated fatty acid can be hydrogenated to very low iodine values.

These methods were developed to produce fatty acids with as high as 90% purities not only from the byproducts of edible fats and oil refining but from the fats and oils themselves. The lauric oils contain fatty acids having 8, 10, 12 and 14 carbon atoms. Soybean, cottonseed and palm oils and tallow are the major sources of fatty acids with 16 and 18 carbon atoms, while fish and rapeseed oils contain 18, 20, 22 and 24 carbon atoms. Fatty acids also are categorized as unsaturated and saturated. The carboxyl group and double bonds in unsaturated fatty acids are the major reaction sites used in the production of fatty acid derivatives such as amines and alcohols, alkanol amides, esters and soaps. Direct consumption of fatty acids in consumer and industrial uses represents about 60% of total fatty acid production.

Purification by distillation, fractionation and hydrogenation is used by fatty acid producers as an integral part of their production plants, but not by edible oil refiners. To increase the volume of acid oil as a starting material for fatty acid production or in laundry and industrial cleaning compounds, the refiner should minimize oil content in the acid oil byproduct. Further efforts to improve the quality of acid oils—especially those recovered from soft oil soapstock—should include removal of color bodies and other interfering contaminants.

Spent clay is another problem material. Its disposal is getting more and more difficult, especially for free standing refineries. Integrated plants have somewhat easier ways of disposing of spent clay. The cake can be slurried either in water or in oil. Water slurries can be added to the meal at the meal drier where the water will be evaporated. Oil slurries should be pumped into the extractor where the oil content can be recovered.

Steam blowing or circulating hot water through the cake still in the filter are more effective for reducing the oil content of the cake than blowing nitrogen or inert gas. The recovered oil might be re-refined or blended with acid oil. Hexane extraction is the most effective method to remove oil from the clay. It might be done while the cake is still in the filter. After the cake is removed from the filter, hexane extraction and clay separation can be achieved in a continuous manner using a cylindrical vessel. This method requires hexane slurry preparation, which is then pumped into the vessel containing water at a proper level. The hexane-oil miscella leaves the tower at the top while the deoiled clay exits at the bottom. Deoiled clay then can be dumped at a landfill.

Deodorization and steam refining generate deodorizer distillate, another important byproduct. The composition of this byproduct varies according to the refining method used to prepare feedstock. Caustic-refined fats and oils contain less free fatty acid than those prepared for steam refining. Equipment design and operating conditions also have an effect on the composition of the distillate.

Free fatty acid contents as low as 25% and as high as 90% are typical for distillates. Distillate from caustic-refined soybean oil contains about 25-35% free fatty acid (FFA), while distillate from steam-refined palm oil contains 80-90% FFA. The low FFA distillate is the preferred starting material to recover tocopherols and sterols from the unsaponifiable fraction of the distillate. The high FFA distillate might be used in feed fat blends and soaps or by fatty acid distillers.

The most valuable compounds in distillates are tocopherols and sterols. Gamma- and delta-tocopherols have antioxidant properties; the alpha-tocopherol is vitamin E. The sterol compounds are used as starting materials for preparation of steroids, such as corticoids, sex hormones, contraceptives and diuretics. All these naturally derived products have to compete with synthesized ones. The demand for natural vitamin E has a tremendous effect on the value of distillate. The tocopherol content and value determine the price of the distillates. Wide fluctuations have been experienced. Sometimes the distillate byproduct is worth three times as much as the finished edible oil product; at other times, it might be worth only as much as the edible oil product.

This is a rather general picture of (a) the major byproducts generated by the most common refining methods for crude fats and oils, and (b) the methods available to refiners to handle their byproducts. I am sure I have not covered all existing possibilities for upgrading and using byproducts from different fats and oils around the world.

In the U.S. and Europe, strict environmental regulations affect the way byproducts may be processed and used. To avoid or minimize problems with wastewater or spent clay, disposal research work is being done, not only on the byproduct itself, but on processing methods that can shift byproduct recovery from one phase of the processing to another and thereby reduce polluting wastes. One example of this is conditioning soybean flakes prior to extraction to produce crude oil that can be degummed to less than 20 ppm phosphorus content. If such an oil is caustic-refined and the soapstock is acidulated, the problem of wastewater treatment is greatly reduced. Some of the degumming methods I have mentioned have the same effect.